SOLUBILITY AND DIFFUSION STUDIES IN ALKALI METALS

FIFTH QUARTERLY REPORT

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SOLUBILITY AND DIFFUSION STUDIES
OF ULTRA PURE TRANSITION ELEMENTS IN
ULTRA PURE ALKALI METALS

FIFTH QUARTERLY REPORT
(June 28, 1964 – October 3, 1964)

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SOLUBILITY AND DIFFUSION STUDIES OF ULTRA PURE TRANSITION ELEMENTS AND COMPOUNDS IN ULTRA PURE ALKALI METALS

By R. L. McKisson and R. L. Eichelberger

I. INTRODUCTION

The purposes of this study are: 1) to define the solution process and determine the equilibrium solubility of highly purified transition metals and selected compounds in highly purified liquid alkali metals, and 2) to measure the diffusion of transition metals and constituents of selected compounds in highly purified liquid alkali metals. The material combinations which are to be considered for both the solution and diffusion studies are: iron, niobium, tantalum, molybdenum, tungsten, zirconium, rhenium, vanadium, hafnium, beryllium oxide, niobium monoxide, tantalum monoxide, zirconium dioxide, zirconium carbide, vanadium monoxide, oxygen-saturated zirconium, and oxygen-saturated hafnium with liquid potassium, and niobium and beryllium oxide with liquid lithium. Specific combinations from the above list will be selected, and it is expected that some combinations will not be investigated.

The studies to be made include the measurement of solubility in the alkali metal at temperatures up to 1200°C, coupled with the investigation of the rate-controlling step and its energy of activation; and the measurement of the liquid state diffusion rate and its energy of activation, also to 1200°C.

It is the goal of this study to develop solubility and diffusion data for well-characterized experimental systems, in which the number and range of complicating variables are minimized, in the hope that such data will not only further the understanding of these processes in alkali metal systems, but will also be of use in the materials selection and design of space electrical power system components.
II. SUMMARY

The potassium purification unit has been completed and can be operated with ease. However, the first batch of distilled potassium product analyzed showed a too-high oxygen level for use in the solubility tests.

Modifications of the manipulators have been made to permit a greater range of adjustment on the vacuum seals on the ball and on the sliding joint. These modifications permit the compensation for wear or flowing of the teflon seal in the ball joint, and of the double O-ring seal on the shaft. With these changes, sampling and handling of the potassium can be performed in a vacuum which remains below \(1 \times 10^{-6}\) Torr. Sampling in the low \(10^{-6}\) Torr range is marginally satisfactory, and quite unsatisfactory at \(1 \times 10^{-5}\) Torr.

Single crystal refractory metal crucibles are not yet available. The contractor who is preparing the crucibles by electrochemically machining them from single crystal stock has experienced severe difficulties in adapting his process (which is satisfactory for poly-crystal) to single crystal materials.

The only satisfactory supplier for 1/2" diameter single crystals of refractory metals is MRC. Metals Research, Ltd. has not yet delivered a usable 1/2" diameter single crystal of Nb or Mo.

Analytical methods have now been verified in the 1-10 ppm range for all of the solute materials in potassium. A satisfactory wet chemical analysis for silicon has not been found. For the present silicon will be determined spectroscopically.
III. TECHNICAL PROGRAM

Environmental Test System

The assembly of the potassium purification unit was completed early in July. Following the assembly, several batches of potassium were used in a rinsing operation so that all of the internal surfaces of the components were brought into contact with either liquid potassium or potassium vapor.

The freeze-seals which are used as on-off valves between the components are found to perform very well, and the movement of potassium through the 1/4" O.D. lines is very easily regulated. In general, the transfer of the metal is readily accomplished using rather small helium pressure differentials. Normally, the one and a half psi differential between 26" Hg vacuum and 29" Hg vacuum is adequate to move the liquid potassium. An operating problem was uncovered in that it was difficult to determine when the proper amount of potassium had been transferred into the filter pot from the supply tank. In the original design, three thermocouples of varying length extended into the chamber. The level of the potassium was to have been detected by sensing the temperature changes occurring as the thermocouples became immersed in the rising potassium. In practice, it was easy to detect the presence of hot potassium at the lowest level, but the responses of the intermediate and upper level thermocouples were not adequate to unambiguously indicate the presence of the potassium at these levels. Since these simple thermocouples have proven to be poor liquid level indicators, they were replaced by two thermocouple wells each of which contains a small heater and a thermocouple. The thermocouple is spark-welded to the inner end of the well. When the heater is operating, and the well is not covered with potassium, the poor heat transfer characteristics of the well cause its temperature to rise 20-30°C above the temperature of the surroundings. Then, as the potassium is transferred into the filter chamber and rises to
contact the end of the well, the excess heat is quickly transferred
away, and the thermocouple emf drops abruptly. The modified unit now
operates very well and gives the required positive response.

In the early testing of the unit, it was convenient to view the
inside of the reflux control condenser by looking through the drop
counter window through the condenser tube using an ophthalmoscope. In
this fashion, condensing potassium could be observed in the reflux
control condenser and it was determined that the rates were in general
agreement with our expectations from the temperature-levels (vapor
pressure-levels) in the distillation column. However, when the tem-
peratures and vapor pressures were high enough to deliver distillate
at the desired rate, there was enough streaming of vapor along the
condenser tube to slowly cloud and cover the sight glass. Because of
the concern that the glass might interact and become an oxygen source
in our collected distillate, a baffle was installed to prevent line-
of-sight streaming.

After the system was rinsed out following these modifications, a
charge of about 200 grams of potassium was distilled into the extruder.
The extrusion of the potassium is readily accomplished using 75 foot-
pounds of torque on the driving screw when the metal is at 25°C, or
using 40 foot-pounds of torque with the potassium at 55°C. The extruded
metal is not a cylinder as was desired, but tends to curl quite markedly.
Further, the surface of the extruded potassium is very sticky, and it
adheres quite tightly to any solid surface so that transferring a
solid sample into a vessel is almost impossible. Because of this, a
stainless steel transfer funnel has been prepared. The extruded
potassium slug will be placed in the heated funnel and the potassium
melted to run down the delivery tube into the single crystal crucible.
The funnel will be cleaned between loadings, unless several samples
are desired in sequence. If this transfer technique proves satis-
factory, the stainless steel funnel will be replaced by one made of
a more inert material, such as Nb-1Zr.
During the course of these operations, it has been found that in time the manipulators develop leaks in the ball joints, and sometimes in the sliding shaft-seal as well. The problem with the ball-joint appears to be that the original teflon chevron-type seal does not have any provision for adjusting the sealing pressure. A modification in the seal has been made so that the clamping ring can be used to adjust the sealing pressure. A marked reduction of the leak rate during movement of the ball has been noted in the two manipulators which have been modified.

The shaft-seal was also modified so that more pressure can be applied to the double O-ring seal. In the original design an approximately 5 pound force is applied by a spring to deform the O-ring to form the seal. The springs are too weak and do not continue to maintain a tight seal. The springs have been replaced by a sleeve which directly compresses the O-rings. Clamping pressure is developed by using screws which can be tightened as required to effect the desired seal pressure. The changes are shown in Figure 1. Re-work of the remaining manipulators will be deferred until more operating experience is obtained to ensure that these modifications continue to be effective during long term use.

With these modifications, a potassium sample can be prepared and loaded into the transfer vessel in a vacuum of <2x10^-6 Torr. When this vacuum level is maintained, the sample does not tarnish during the handling procedure. However, in earlier sampling attempts in which the pressure rose to 1x10^-5 Torr, the potassium developed a pale blue tarnish whose intensity was quite sensitive to pressure, and also to the time of exposure.

Figure 2 shows the sample cut-off operation using the tungsten wire "cheese-cutter." Figure 3 shows the sample in position above the mouth of the transfer vessel. When the tungsten wire is heated the sample, free of any contaminants, drops into the vessel. The vessel is sealed by seating the tapered joint in the cap to that on the vessel. Both photographs were taken through the viewing port when the chamber was under an operating vacuum of 8x10^-7 Torr.
Material Procurement, Preparation, and Characterization

The single crystal samples of molybdenum, tantalum, and niobium submitted to Sifco Metachemical in Cleveland for electrochemical machining into crucibles have not yet been returned. Sifco is behind schedule on delivery because these single crystal materials behave much differently in their electrochemical process than does polycrystalline stock. They are carrying out a series of modifications of their process in an attempt to develop a satisfactory method, and report in a telephone conversation that they believe that they are close to a solution of the problem. However, if the difficulties in obtaining satisfactory single crystal crucibles cannot be overcome in time for use in the first experiments, high purity zone-refined polycrystalline sample crucibles will be used.

In June, three molybdenum single crystals were received from Metals Research, Ltd. Their specifications called for an 0.45 inch minimum diameter, but the crystals were typically 0.35-0.40 inches in diameter and not usable. A telephone conversation with the MR agent regarding these undersize parts elicited the comment that they observe a decrease in crystal diameter each time they make a zone-refining pass, but the amount of diameter change is very difficult to predict and control. Two of these undersized crystals have been returned.

Recently, three additional molybdenum single crystals were received from Metals Research, Ltd., but they were quite irregular in shape. The diameters ranged from 0.50" to 0.40" along the three-inch length, so that they are not usable.

Two niobium single crystals were received from Metals Research, Ltd. Both were undersize, even though the importance of external size and straightness was previously emphasized to their sales representative in a telephone conversation. The crystals were returned. At present, therefore, we have not received any usable crystals from Metals Research, Ltd.
One 0.45" + diameter, four inch long molybdenum single crystal and one 1/2" diameter, four inch long zone refined polycrystalline iron sample have been received from Materials Research Corporation (MRC). Both samples are usable. One inch will be removed from each for use in making a spot-check of impurity level of these MRC materials.

The technique for electropolishing the inside of the iron crucibles was perfected. An applied voltage of 9 volts and a current range of 20 to 30 amps was used. The principal problem in this study has been to achieve a balance between electrolyte flow and electrode size so that the electrode does not short out to the wall, and does maintain a non-polarizable character. The areas of the polished crucibles were measured by the DLC technique using the standard sample area calibration of 10 μf/sq cm and are shown in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Geometric Area cm²</th>
<th>DLC 'Area' cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.6</td>
<td>19.6</td>
</tr>
<tr>
<td>2</td>
<td>19.2</td>
<td>20.8</td>
</tr>
</tbody>
</table>

These data indicate that for the electropolished iron crucibles the ratio, DLC Area/Geometric Area, is 1.0, within 8%. This procedure is described by Argue, et al, in "Double Layer Capacitance Measurements on Iron Crucibles to Determine Surface Area," AI-TDR-64-229.

Chemical Analysis

The analytical chemistry support effort requires the determination of the solute metals in potassium at low levels with high precision, and the verification of purity of the solvent potassium and solute metals. During this quarter, the effort has been directed toward the verification of additional analytical methods, the study of analytical procedures for silicon, the analysis of tantalum crucible material, and the analyses of the potassium product for oxygen and sodium. The status of the analytical support program is shown in Tables 4, 5, 6, and 7 in the Appendix.
Methods have now been verified in the 1-10 ppm range for all of the solute materials in potassium. Adequate sensitivity for the determination of sodium in potassium by flame photometry has been demonstrated; 1-50 ppm of sodium in potassium can be determined with a precision of better than ±0.2 ppm. The accuracy is dependent upon the sodium content of the "standard" potassium and the sodium content of water used as a solvent.

Several approaches to the problem of determining silicon by wet chemistry techniques in niobium, tantalum, and molybdenum have been investigated. None of the state of the art methods tested to date provides adequate sensitivity or accuracy for the determination of silicon in the <20 ppm range in these metals. For the present, silicon will be determined spectroscopically.

Methods for the determination of niobium and molybdenum in tantalum have been verified and the two MRC tantalum samples on hand have been analyzed. A summary of the results for the analysis of tantalum is shown below.

Table 2
Analyses of Impurities in Single Crystal Tantalum

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Vendor's Typical Analysis (ppm)</th>
<th>Chemical Analysis (AI) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>&lt;10</td>
<td>10 ± 0.3</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>&lt;10</td>
<td>7 ± 0.5</td>
</tr>
<tr>
<td>Niobium</td>
<td>&lt;20</td>
<td>21 ± 0.7</td>
</tr>
<tr>
<td>Silicon</td>
<td>not reported</td>
<td>Verification of Procedure in progress</td>
</tr>
</tbody>
</table>

A number of familiarization analyses of oxygen in potassium were made using potassium collected during our purification unit clean-up processing. This material showed oxygen contents ranging up to about 100 ppm, measured by the mercury amalgamation technique on liquid samples pipetted from beneath the surface of the metal. Analyses of
the potassium product collected in the extruder were also made. As
is noted above, severe sampling difficulties were encountered and some
samples became contaminated during sampling and subsequent handling.
Their analyses are, of course, erratic and of little consequence. The
analyses of the samples which showed no evidence of tarnishing are
shown in Table 3, together with the most recent set of three oxygen
analyses of the waste potassium.

Table 3

<table>
<thead>
<tr>
<th>Date of Analysis</th>
<th>Oxygen Content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8/24/64 (samples cut from waste K in inert atm. box)</td>
<td>68, 78, 94</td>
</tr>
<tr>
<td>9/17/64</td>
<td>40, 36</td>
</tr>
<tr>
<td>9/18/64</td>
<td>70</td>
</tr>
<tr>
<td>9/29/64</td>
<td>65, 71</td>
</tr>
</tbody>
</table>

The differences in oxygen level between 9/17 and 9/29 cannot be ex-
plained, but, in any event, the first batch of collected potassium
has a too-high oxygen content for use in the solubility tests.
Accordingly, a second batch is being prepared.

The product potassium has been analyzed for sodium with the
following result:

1) By spectrograph (three samples): <5, 2, and 1 ppm Na
2) By absorption spectrophotometry (two samples): 6.4 and 3.1
ppm Na.

The sodium analysis quoted by Mine Safety Appliance Research Corp. for
the as-received potassium is 30 ppm Na. It is evident, therefore, that
purification with respect to sodium is being achieved in the purifica-
tion process.
IV. NEXT REPORT PERIOD ACTIVITIES

During the next quarter, the major effort will be directed toward preparing potassium of adequately low oxygen content and toward carrying out experimental measurements on the polycrystalline iron samples; and on the single crystal niobium, molybdenum, and tantalum samples, or, if necessary, on high purity polycrystalline niobium, molybdenum, and tantalum samples.
Figure 1. Manipulator Modifications

1. Cut teflon chevron seal to form two separate parts. Clamping pressure can now be applied to teflon lips.
2. Added spacer under ring to transmit clamping pressure.
3. Spacer which replaces spring
4. Screws added (4 ea) to apply pressure to O-rings
5. Pump-outs
Figure 2. Sample Cutting with the "Cheese-Cutter"
Figure 3. Sample Loading
V. REPORTS ISSUED ON THIS CONTRACT


### IV. APPENDIX

#### TABLE 4

**Analytical Method for Determining "Interstitial" Impurities**

<table>
<thead>
<tr>
<th>Element to be Determined</th>
<th>Method and Description</th>
<th>Sensitivity (a) and Remarks</th>
<th>Ref.</th>
<th>Status of Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen Solute</td>
<td>Micro inert gas fusion or vacuum fusion. Oxygen converted to CO₂ which will be determined manometrically or by gas chromatography.</td>
<td>No firm limits of sensitivity can be established on the basis of published literature. Possibly a sensitivity in the range of 5-10 micro grams can be achieved. However, equipment and reagent blank corrections lie in this range, making accuracy and precision difficult to maintain. A sensitivity of 0.3 micro gram has been reported.</td>
<td>1,2, Since this method is in routine use at AI it was not verified specifically for this project. A lower useful limit of 10 ppm O₂ has been achieved. Although a precision of ±1 ppm is observed, the absolute accuracy has not been proved because adequate standards are not available.</td>
<td>3,4, 5</td>
</tr>
<tr>
<td>Solvent</td>
<td>Mercury amalgamation of the alkali. Oxide residue recovered and titrated with standard acid; or sodium in the oxide residue can be determined by flame photometry. See note (b) regarding oxygen in lithium.</td>
<td>5 ppm ± 40%, estimate, based on the determination of oxygen in sodium at AI.</td>
<td>6,7. Equipment and procedure tested, using sodium, at the 15 ppm level. Precision is ±2.5 μg. Greater sensitivity is available but there are no adequate standards available to verify the method at lower oxygen levels.</td>
<td>8,9, 10</td>
</tr>
<tr>
<td>Nitrogen Solute</td>
<td>Micro Kjeldahl. Nitrogen is converted to ammonia which is determined spectrophotometrically with Nessler's Reagent.</td>
<td>1-2 micro grams</td>
<td>11. The procedure is in routine use at AI and, therefore, not verified specifically for this project.</td>
<td>11</td>
</tr>
<tr>
<td>Solvent</td>
<td>Micro Kjeldahl.</td>
<td>1.0 ppm</td>
<td>12,13. Procedure verified using sodium: Range 1-5 ± 0.2 ppm.</td>
<td></td>
</tr>
<tr>
<td>Hydrogen Solute</td>
<td>High temperature vacuum extraction of hydrogen which is then determined manometrically or by gas chromatography.</td>
<td>1.0 micro gram</td>
<td>14,15 Method is used semi-16,17 routinely at AI, therefore, verification for this project was not necessary, 1 ppm H₂ can be determined. Use of mass spectrometer readout is being investigated.</td>
<td></td>
</tr>
<tr>
<td>Solvent</td>
<td>High temperature extraction in iron capsule. Hydrogen diffuses from capsule and is determined manometrically or by gas chromatography.</td>
<td>1.0 ppm</td>
<td>18 Same as above.</td>
<td></td>
</tr>
<tr>
<td>Carbon Solute</td>
<td>Micro combustion to CO₂ which is determined manometrically or by gas chromatography.</td>
<td>1-10 micro grams. Equipment and reagent blanks limit precision and accuracy.</td>
<td>19,20 This technique (utilizing conductometric readout) is used routinely at AI for samples containing more than 50 ppm C. No verification for lower range.</td>
<td></td>
</tr>
<tr>
<td>Solvent</td>
<td>Wet oxidation to CO₂ which is then determined by gas chromatography.</td>
<td>2 ppm; at this level good accuracy and precision are not expected. No firm data available.</td>
<td>22,23 Accuracy and sensitivity limited by reproducibility of the reagent blank which can be determined to a precision of ±5 μg. No material has been analyzed which contains less than 10 ppm C.</td>
<td></td>
</tr>
<tr>
<td>Dry oxidation.</td>
<td>5-25 micro gram in 0.2 gram 24 sample of Na. 2.0 ± 0.4 micro gram determined in pure Na.</td>
<td></td>
<td>Not tested at AI.</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 4 (continued)

| Sulfur Solute | Wet oxidation to sulfate followed by reduction to sulfide which is determined spectrophotometrically with p-amino-dimethylaniline. | 1.0 micro gram | 25 Method is used at AI on occasional samples. Sensitivity to 1.0 μg has been demonstrated. |
| Solvent | Same as above. | 1 ppm | 25 Procedure has not been verified in a potassium matrix. |

| Phosphorous Solute | Convert to phosphate and determine spectrophotometrically as molybdenum blue. | 2 micro grams | 26, 27 Method is used routinely at AI and, therefore, was not verified for this project. |
| Solvent | Same as above. |

NOTES: (a) Sensitivity is used here to mean the lowest concentration or amount of a substance which can be determined routinely with reasonable accuracy and precision. Except as noted in the Table, data on accuracy and precision which are applicable to the concentration range or to the system of interest are not available in the literature. In these cases, limits of "reasonable" accuracy must be established.

(b) No satisfactory method for determining oxygen in lithium is reported in the literature. The amalgamation method applicable to sodium and potassium is not suitable for the analysis of lithium. The method of Jawcrowski and Potts based on dissolving the alkali in liquid ammonia with the subsequent separation of insoluble oxide is as yet unproved. The best methods reported are those based on activation analysis. According to Bate, the fast neutron reaction, \( ^{16}\text{O} + n \rightarrow ^{16}\text{N} \) can be used to determine approximately 10 ppm of oxygen, and the reaction, \( ^{16}\text{O} (\gamma, n) ^{15}\text{O} \), can detect \( 10^{-2} \) to \( 10^{-6} \) grams of oxygen depending on the beam strength available. An activation method based on the reactions, \( ^{6}\text{Li} + n \rightarrow ^{4}\text{He} \) and \( ^{16}\text{O} + n \rightarrow ^{18}\text{F} \) should prove especially suitable for the determination of oxygen in lithium. \(^{18}\text{F} \) can be determined by beta counting or gamma counting of the annihilation radiation (\(^{18}\text{F} \) decays by position emission). Sensitivities below 1 ppm might be achieved.
<table>
<thead>
<tr>
<th>Element to be Determined</th>
<th>Method and Description</th>
<th>Sensitivity (in micro grams) and Remarks</th>
<th>Ref.</th>
<th>Status of Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Spectrophotometric with o-phenanthroline</td>
<td>0.01-5.0 (± 2%)</td>
<td>30,31</td>
<td>Method verified in potassium matrix: 1-10 ppm ± 2%</td>
</tr>
<tr>
<td>Niobium</td>
<td>Spectrophotometric as the reduction product of the complex molybdo-niobate</td>
<td>0.1-10 (above 1 ppm ± 2%)</td>
<td>32</td>
<td>Method utilizing ammonium thiocyanate as the chromogenic agent was verified in potassium matrix. Range, 1-10 ppm ± 5%</td>
</tr>
<tr>
<td>Tantalum</td>
<td>Spectrophotometric with malachite green</td>
<td>1-2 (to better than ±5%; estimate)</td>
<td>33</td>
<td>Method verified in potassium matrix. Range 1-10 ± 5%</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Spectrophotometric as the thiocyanate, or dithiol complex</td>
<td>1.0 (± 2%)</td>
<td>34,35,36</td>
<td>Method verified in potassium matrix. Range 1-10 ± 2%</td>
</tr>
<tr>
<td>Tungsten</td>
<td>Spectrophotometric as the dithiol complex</td>
<td>1.0 (to better than ± 5%; estimate)</td>
<td>36</td>
<td>Method verified in potassium matrix. Range 1-10 ± 4%</td>
</tr>
<tr>
<td>Rhenium</td>
<td>Spectrophotometric as the thiocyanate or for greater sensitivity by the reduction of sodium tellurate under the influence of Re</td>
<td>1.0 (to better than ± 5%; estimate)</td>
<td>37,38</td>
<td>Method using ammonium thiocyanate as the chromogenic agent was verified in potassium matrix. Range 1-10 ± 5%</td>
</tr>
<tr>
<td>Zirconium</td>
<td>Spectrophotometric with 1-(2-pyridylazo)-2-napthol (PAN complex)</td>
<td>1.0 (± 5%; estimate)</td>
<td>40</td>
<td>Method using pyrocatechol violet verified in potassium matrix. Range 1-20 ± 5%</td>
</tr>
<tr>
<td>Vanadium</td>
<td>Spectrophotometric as the 8-hydroxyquinolinate</td>
<td>0.1 (above 1 ppm ± 2%)</td>
<td>41,42</td>
<td>Method verified in potassium matrix. Range 1-10 ± 5%</td>
</tr>
<tr>
<td>Hafnium</td>
<td>Spectrophotometric with 1-(2-pyridylazo)-2-napthol</td>
<td>2.0 (± 5%; estimate)</td>
<td>40</td>
<td>Method using pyrocatechol violet was verified in a potassium matrix. Range 2-20 ± 5%</td>
</tr>
<tr>
<td>Material to be Analyzed</td>
<td>Description of Method</td>
<td>Typical Impurities and Reported Limits of Detection</td>
<td>Ref.</td>
<td>Status**</td>
</tr>
<tr>
<td>------------------------</td>
<td>------------------------</td>
<td>--------------------------------------------------</td>
<td>------</td>
<td>----------</td>
</tr>
<tr>
<td>Potassium and Lithium</td>
<td>Flame Photometry</td>
<td>Other alkali metals can be determined with high accuracy and precision at concentrations near 1 ppm.</td>
<td>43</td>
<td>Atomic absorption spectrophotometry used in place of flame analysis for determination of Na. Method verified in range of 1-50 ppm ± 0.2 in KCl matrix. Samples analyzed contained 6.4 and 3.1 ppm Na.</td>
</tr>
<tr>
<td></td>
<td>Emission spectroscopy -</td>
<td>1 ppm - Mo, Mn, V</td>
<td>44, 45</td>
<td>Two potassium samples were analyzed. No heavy metals found. Samples converted to chloride. Sodium content was less than 2 ppm. A trace of Ca was indicated but not determined (&lt; 5 ppm). (A third sample contained less than 5 ppm Na.)</td>
</tr>
<tr>
<td></td>
<td>Samples converted to sulfates, fused, fined ground, mixed with graphite, d.c. arc, graphite cup.</td>
<td>1-2 ppm - W, Cr, Ni, Fe</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 ppm - Zn</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 ppm - Ta, Nb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>Emission Spectroscopy -</td>
<td>1-10 ppm - B</td>
<td>46</td>
<td>Samples from polycrystalline iron crucible material analyzed (as metal). Only impurities found were Mg, Si and Mn, all at concentrations of less than 5 ppm.</td>
</tr>
<tr>
<td></td>
<td>direct analysis of metal</td>
<td>10-50 ppm - Al, Co, Cu, Cr, Mn, Mo, Ni, Pb, Si, Sn, Ti, V</td>
<td>47, 48, 49</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sample using spark technique; or metal sample converted to oxide, mixed with graphite and analyzed.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Niobium and Tantalum</td>
<td>Emission Spectroscopy -</td>
<td>1 ppm - B</td>
<td>50</td>
<td>Analysis of two samples (oxide form) from tantalum single crystals showed only Fe (&lt; 50 ppm), Nb (&lt;100 ppm), and Si (150 ± 75 ppm) as impurities. Niobium samples not analyzed.</td>
</tr>
<tr>
<td></td>
<td>sample converted to oxide, Li2CO3 used as a buffer, and Ta as internal standard, d.c. arc; or carrier distillation method, oxide plus Ga2O3.</td>
<td>10 ppm - Al, Cd, Cr, Co, Fe, Mn, Mo, Ni, Si, Sn, Ti, Zr</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>250 ppm - Ta (in Nb)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 6 (continued)

Molybdenum  | Emission Spectroscopy - samples buffered with graphite mixtures containing internal standard of Cu or Ni, both high voltage a.c. arc and d.c. arc used.  
| 1 ppm - Ca, Cu, Mg, Mn  
| 4 ppm - Ba, Na  
| 5 ppm - Al, Fe, Si  
| 6 ppm - Cr, Ni  
| 8 ppm - Sn  
| 10 ppm - K, Sr  
| 100 ppm - W  
  
Tungsten  | Emission Spectroscopy - carrier distillation, W converted to oxide, AgCl used as carrier with Co as internal standard, or with Ga₂O₃ as carrier.  
| 0.5 ppm - Cu, Si  
| 1.0 ppm - Al, Na, Ni  
| 5.0 ppm - Cr, Fe, K, Sn  
| 10 ppm - Mo  
  
Rhenium  | Emission Spectroscopy - convert to oxide and utilize carrier distillation; or dissolve in HNO₃, add carbon, evaporate, and arc residue.  
| 1 ppm - Bi, Cd, Pb, Sn  
  
Zirconium and Hafnium  | Emission Spectroscopy - metal filings or oxides are excited with either a.c. or d.c. arcs, graphite electrodes.  
| Some 22 elements determined at concentrations below 10 ppm with accuracy of ± 30%  
  
Hafnium in Zirconium  | With use of barium fluoride flux  
| Hafnium to 30 ppm in zirconium  
  
Spectrographic analysis (using metal) showed that samples from two single crystals contained only Fe (< 50 ppm) and Si (< 10 ppm) as impurities.
Zirconium With use of 12-a, d.c. arc technique in Hafnium Zirconium to 10 ppm in hafnium

Vanadium Convert to oxide and mix with graphite 1-10 ppm - Al, Bi, Fe, Si, Cd, Mn, Mg, Cu, As, Sb

* Spectrographic analyses to be used as a basis for selecting analyses to be performed chemically. See next table.

**Most of the techniques described are used at AI. Verification was limited to materials where actual samples were on hand. The most serious problem encountered is that of pure standards: Materials used on this project are of higher purity than our spectrographic standards, thereby limiting applicability. "Less than" values reported in most cases.
<table>
<thead>
<tr>
<th>Matrix Element</th>
<th>Element Determined</th>
<th>Method</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Copper</td>
<td>Biquinoline</td>
<td>Method verified in the range of 1-10 ppm. Sample has not been analyzed due to failure to detect this impurity by spectrographic analysis and a desire to limit expenditures.</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Thiocyanate</td>
<td></td>
<td>Method has been verified in the range 1-10 ppm ± 5%. Work on sample discontinued.</td>
</tr>
<tr>
<td>Silicon*</td>
<td>Permanganate</td>
<td></td>
<td>Several methods tested. None satisfactory at concentrations near 10 ppm.</td>
</tr>
<tr>
<td>Manganese</td>
<td></td>
<td></td>
<td>Method verified in range of 1-10 ppm. Sample analyzed and found to contain less than 0.5 ppm Mn.</td>
</tr>
<tr>
<td>Niobium</td>
<td>Tantalum</td>
<td>Malachite Green</td>
<td>Work on method discontinued.</td>
</tr>
<tr>
<td>Iron</td>
<td>Ortho-phenanthroline</td>
<td></td>
<td>Method verified in the range 1-10 ppm ± 5%. Two samples analyzed (11.8 and 11.2 ppm).</td>
</tr>
<tr>
<td>Silicon*</td>
<td>Molybdenum blue</td>
<td></td>
<td>Initial verification work shown to be incorrect. Method is not satisfactory. Work discontinued.</td>
</tr>
<tr>
<td>Tantalum</td>
<td>Iron</td>
<td>Batho-phenanthroline</td>
<td>Method verified in the range of 1-10 ppm ± 5%. Two samples analyzed. (10.0 ± 0.3 ppm and 6.0 ± 0.3 ppm)</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Dithiol</td>
<td></td>
<td>Method verified in the range 3-25 ppm to better than ± 10%. Two samples analyzed (7.0 ± 0.5 ppm and 10.0 ± 0.5 ppm)</td>
</tr>
<tr>
<td>Niobium</td>
<td>Thiocyanate</td>
<td></td>
<td>Method verified in the range of 2-12 ppm ± 5%. Two samples analyzed. (21.0 ± 0.7 ppm and 8.2 ± 0.7 ppm)</td>
</tr>
<tr>
<td>Silicon*</td>
<td></td>
<td></td>
<td>No satisfactory method. Several tested.</td>
</tr>
<tr>
<td>Element</td>
<td>Method</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>-------------</td>
<td>-------------------------------</td>
<td>-------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Batho-phenanthroline</td>
<td>Method verified in the range of 1-10 ppm ± 5%. Two samples analyzed (6.0 ± .2 ppm and 5.0 ± .2 ppm)</td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Niobium</td>
<td>4-(2-pyridylazo-resorcinol), PAR</td>
<td>Method verified in range of 5-30 ppm ± 5%. No samples analyzed.</td>
<td></td>
</tr>
<tr>
<td>Silicon*</td>
<td></td>
<td>Several methods tested. None satisfactory in range of interest.</td>
<td></td>
</tr>
</tbody>
</table>

*There is a need for research which will provide satisfactory methods for the determination of silicon at levels near 10 ppm.*
References for Tables 4, 5, 6, and 7

26. ASTM E30-60T.


